J Ex. in Dok.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : D01F 8/04, 8/12, 8/14, A46D 1/00, D01D 5/253 — A1

(11) International Publication Number: WO 97/14830

(43) International Publication Date: 24 April 1997 (24.04.97)

(21) International Application Number: PCT/US96/16293

(22) International Filing Date: 11 October 1996 (11.10.96)

(30) Priority Data:
60/005,542 18 October 1995 (18.10.95) US
Not furnished 27 September 1996 (27.09.96) US

(71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors: RACKLEY, Robert, Lee; 119 Canterbury Drive, Parkersburg, WV 26101-8048 (US). NELSON, Charles, Fletcher; 67 Wildwood Drive, Parkersburg, WV 26101-9661 (US).

(74) Agent: KRUKIEL, Charles, E.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

(81) Designated States: CN, JP, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: COEXTRUDED MONOFILAMENTS

(57) Abstract

This invention relates to a coextruded monofilament having a core material made of a first resin and a sheath material made of a second resin, with the second resin being different from the first resin, and a pocket formed in the end of the monofilament. This invention also relates to a method of forming a pocket in the end of a coextruded monofilament by chemical or mechanical means, or a combination of chemical and mechanical means.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	**GB**	United Kingdom	**MW**	Malawi
AT	Austria	**GE**	Georgia	**MX**	Mexico
AU	Australia	**GN**	Guinea	**NE**	Niger
BB	Barbados	**GR**	Greece	**NL**	Netherlands
BE	Belgium	**HU**	Hungary	**NO**	Norway
BF	Burkina Faso	**IE**	Ireland	**NZ**	New Zealand
BG	Bulgaria	**IT**	Italy	**PL**	Poland
BJ	Benin	**JP**	Japan	**PT**	Portugal
BR	Brazil	**KE**	Kenya	**RO**	Romania
BY	Belarus	**KG**	Kyrgystan	**RU**	Russian Federation
CA	Canada	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CF	Central African Republic			**SE**	Sweden
CG	Congo	**KR**	Republic of Korea	**SG**	Singapore
CH	Switzerland	**KZ**	Kazakhstan	**SI**	Slovenia
CI	Côte d'Ivoire	**LI**	Liechtenstein	**SK**	Slovakia
CM	Cameroon	**LK**	Sri Lanka	**SN**	Senegal
CN	China	**LR**	Liberia	**SZ**	Swaziland
CS	Czechoslovakia	**LT**	Lithuania	**TD**	Chad
CZ	Czech Republic	**LU**	Luxembourg	**TG**	Togo
DE	Germany	**LV**	Latvia	**TJ**	Tajikistan
DK	Denmark	**MC**	Monaco	**TT**	Trinidad and Tobago
EE	Estonia	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**UG**	Uganda
FI	Finland	**ML**	Mali	**US**	United States of America
FR	France	**MN**	Mongolia	**UZ**	Uzbekistan
GA	Gabon	**MR**	Mauritania	**VN**	Viet Nam

TITLE

COEXTRUDED MONOFILAMENTS

This application claims the benefit of U.S. Provisional Application No. 60/005,542, filed October 18, 1995.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to coextruded monofilaments which may be used, for example, in bristles for toothbrushes.

2. Description of the Related Art

Bristles made from nylon 6,12 or from polyester are typically circular in cross section with the ends of the bristles being well rounded. When used in toothbrushes, the rounded ends have been preferred because using bristles with rounded ends have a lower tendency to damage soft and hard oral tissue.

SUMMARY OF THE INVENTION

This invention relates to a coextruded monofilament having a core material made of a first resin and a sheath material made of a second resin, with the second resin being different from the first resin, and a pocket formed in the end of the monofilament.

This invention also relates to a method of forming a pocket in the end of a coextruded monofilament by chemical or mechanical means, or a combination of chemical and mechanical means.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a view in cross sectional view in elevation of a coextruded monofilament made in accordance with this invention;

Figure 2 is a top plan view of the coextruded monofilament of Figure 1;

Figure 3 is a view in elevation of a conventional monofilament;

Figure 4 is a top plan view of the conventional monofilament of Figure 3;

Figure 5 is a scanning electron microscope photograph at a magnification of 318x of a pocket formed in the end of a coextruded monofilament of this invention;

Figure 6 is a 50x magnified photograph of a pocket formed in the end of a coextruded monofilament of this invention;

Figure 7 is a scanning electron microscope photograph at a magnification of 242x of a pocket formed in the end of a coextruded monofilament of this invention;

Figure 8 is a magnified photograph of a pocket formed in the end of a coextruded monofilament of this invention;

Figure 9 is a scanning electron microscope photograph at a magnification of 158x of a pocket formed in the end of a coextruded monofilament of this invention; and

Figure 10 is a magnified photograph at a magnification of 419x of a pocket formed in the end of a coextruded monofilament of this invention.

DETAILED DESCRIPTION

This invention relates to a coextruded monofilament of a core material made from a first resin, and a sheath material made from a second resin, wherein the second resin is different from the first resin, and wherein the coextruded monofilament has a pocket formed in the end of the coextruded monofilament. The purpose of this pocket is to hold a material, such as a cleaning material, so that the cleaning material in the monofilament has a longer contact with the surface to be cleaned than if the

cleaning material was on the rounded end of a conventional monofilament. For example, if the coextruded monofilament is used in a toothbrush bristle, the pocket will hold toothpaste in contact with a tooth longer than a coextruded monofilament with a conventional rounded end.

A used herein, the term "core" refers to the central portion of the coextruded monofilament as examined at a cross section. As used herein, the term "sheath" refers to an outer coating layer or layers over the core material on a coextruded monofilament.

Examples of combinations of sheath and core materials include a sheath material of nylon 6; 6,6; 6,10; 6,12; 6,9; 11; 12; copolymers of 6/6,6; 10,10 nylon; and mixtures thereof, and a core material of a copolyester ether such as that sold under the trademark Hytrel® by E.I. du Pont de Nemours and Company of Wilmington, Delaware.

Other examples of combinations of sheath and core materials include a sheath material of a nylon, a polyester, especially polyethylene terephthalate (PET) or polybutylene terephthalate (PBT), a polyurethane, polyvinylidene chloride, or mixtures thereof, and a core material of polyvinyl chloride, polyvinyl acetate copolymer, polystyrene, or mixtures thereof.

There is no limitation on the shape of the cross section of either the core or the sheath of the coextruded monofilament. Either or both may be circular, triangular, square, pentagonal, hexagonal, oval, lobate, triocular, tetraocular or any other shape.

The coextruded monofilament may be made by conventional methods known in the art, such as is disclosed in U.S. Patent No. 5,313,909. It is important that the core and sheath be made from different materials in order to obtain all the benefits of the present invention.

The pocket in the monofilament may be made by mechanical, or by chemical means, or by a combination of mechanical and chemical means.

One method for making the pocket in the end of the monofilament is to abrade the ends of the monofilament with, for example, a fine stainless steel brush in order to form the pocket. An abrasion resistant additive such as polyethylene, silicone oil, or mineral additives such as talc or titanium dioxide may be added to the sheath material so that the core material is preferentially abraded by the mechanical means.

Another method of forming the pocket is by bringing the end of the monofilament into contact with a solvent which will dissolve or degrade the core material, but not the sheath material, in order to form the pocket in the end of the monofilament. The time the monofilament is in contact with the solvent and the temperature of the solvent both affect on the depth of the pocket.

If the core material is a copolyester ether, then a suitable solvent is methylene chloride, antine, carbon tetrachloride, chlorosulfonic acid, ethyl chloride, ethylene dichloride, hydrazine, 37% hydrochloric acid, perchloroethylene, phenol, nitric acid, sulfuric acids, or 110F steam. Most of these solvents have little effect on nylons especially for short exposure times.

If the core material is a polyvinyl chloride, polyvinyl acetate copolymer, polystyrene, or mixtures thereof, then a suitable solvent is acetone.

Other examples of sheath and core polymers are a sheath polymer of nylon 6,10 or nylon 6,12 with a core polymer of nylon 6 or nylon 6,6. For such a coextruded monofilament, dilute hydrochloric acid is a suitable solvent to be used to form a pocket in the end of the coextruded monofilament.

Another example of a coextruded monofilament of this invention is a sheath polymer of nylon 6,12 and a core polymer of nylon 6,10. A 90% formic acid solution is a suitable solvent to be used to form a pocket in the end of the coextruded monofilament.

Another way to form the pocket in a coextruded monofilament is to add a ultraviolet light inhibitor to the sheath polymer but not the core polymer, and expose the coextruded monofilament to intense ultraviolet light to preferentially degrade the core in the end of the coextruded monofilament. The coextruded monofilament may then be subject to further mechanical treatment, if necessary, to form the pocket to desired proportions.

The depth of the pocket should be from about 0.001 to 0.250 inches (0.025 to 6.4 millimeters).

The diameter of the coextruded monofilament should be from about 0.001 to 0.100 inches (0.025 to 2.5 millimeters), and the ratio of the area of

the core to the area of the coextruded monofilament should be from about 0.1 to about 0.9, with a preferred ratio being from about 0.25 to about 0.75.

The monofilaments may be grouped together in tufts, and attached to a brush. Examples of the types of brush in which these monofilaments may be used include a toothbrush, and a paintbrush, but this invention is not limited to any specific type of brush, and may be used in any type of brush.

The ends of the coextruded monofilaments of this invention may be flagged by conventional means. The term "flagging" means that the ends of the inventive coextruded monofilaments having pockets form in their ends may be split by conventional means from the end of the monofilament to the bottom of the pocket to form what are known as "flags" in the ends of the monofilament. These flags include a concave portion of the pocket and provide the same benefits as the coextruded monofilaments having pockets in the ends that are not flagged.

EXAMPLES

Example 1

Coextruded monofilaments having a core of Hytrel® 4056 copolyester ether and a sheath of nylon 612 were made using conventional methods. The monofilament was conditioned at 125°C by backwinding it through a conditioner on a spinning line and then processed into hanks. The cross sectional area of the core was 25% of the total cross sectional area of the monofilament.

These coextruded monofilaments were tufted into a tuft toothbrush and the ends of the monofilaments were subjected to conventional end rounding.

A fine stainless steel brush having 0.003 inch stainless steel bristles was used to abrade the ends of the coextruded monofilaments in the tufts for about 2-3 minutes to form pockets in the end of the monofilaments as is shown in Figure 7.

The stainless steel brush was 3 inches (76.2 mm) in diameter and was rotated at 1200 rpm. About 0.5 inches (12.7 mm) interference between the stainless steel brush and the bristles was used. Hence the sides and ends of the bristles were abraded but since the core material was a

softer resin a small 0.002 inch deep pocket was formed in the end of the bristle.

Example 2 - Comparative Example

A coextruded monofilament having a core of PET and a sheath of nylon 6,12 was made as in Example 1, except that the conditioning temperature was 175°C. The cross sectional area of the core was 50% PET. A higher conditioning temperature was used than in Example 1 because the melt point of the Example 1 core was 150°C and the PET core of this Example had a higher melt point of 255°C so a standard nylon 6,12 conditioning temperature was used.

The bristles were processed into toothbrushes like Example 1 and were subjected to a similar mechanical treatment with a stainless steel brush. However in this example no pockets were formed because the PET core was not preferentially abraded. Hence the bristle tip had a profile like that as shown in Figure 3. A combined mechanical and chemical treatment would be required to form a pocket in the end of the coextruded monofilament having a sheath-core combination of this Example.

Example 3

A coextruded monofilament having a sheath of nylon 6,12 and a core of PBT was made as in Example 2. The cross sectional area of the sheath was 70% of the cross sectional area of the monofilament.

Toothbrushes were made from the coextruded monofilaments as in Examples 1 and 2, and the ends of the monofilaments were abraded with a stainless steel brush for about 2-3 minutes. As may be seen in Figure 5, the monofilaments had an appearance similar to the monofilaments of Example 1 although the pocket formed was not as deep as in Example 1. The 70% core did cause a wider pocket to be formed than the pocket in Example 1.

Example 4

Coextruded monofilaments were made as in Example 1 and were bundled together into approximately two inch diameter bundles. The ends of the coextruded monofilament in the bundle were abraded with the

same stainless wire brush as used in Example 1, except that the abrasion took place for about 15 minutes. The center sections of the coextruded monofilaments were indented as in Example 1 to form a pocket which demonstrated that the coextruded monofilaments of this invention may be processed as bundles as well as toothbrushes.

Example 5

Toothbrushes having coextruded monofilaments were made as in Example 1, but were treated chemically rather than mechanically. The ends of the coextruded monofilaments of a toothbrush were exposed to methylene chloride for about 12 minutes, which is a strong solvent for Hytrel® copolyester ether but is not a solvent for nylon 612. The cores of the ends of the coextruded monofilaments were dissolved to form pockets, and the coextruded monofilaments were subjected to mechanical abrasion for about 1-3 minutes to smooth the ends of the monofilaments. Photographs of the bristles are shown in Figure 6 and Figure 8.

Example 6

A bundle of coextruded monofilaments was made as in Example 4, and the ends of the monofilaments were treated by dipping the ends into a shallow bath of methylene chloride for about 10 minutes to form pockets in the ends of the monofilaments. The ends of the monofilaments were subjected to mechanical treatment with the stainless steel brush of Example 1 to round the ends of the monofilaments. These bristles are shown at a magnification of 158x in Figure 9 and a magnification of 419x in Figure 10. By comparison of the depth of the pocket to the width it was estimated that the pocket formed in this Example was about 0.004 inches (0.1 mm) deep.

Example 7 - Comparative Example

A coextruded monofilament was made having a nylon 6, 12 sheath and a nylon 6, 12 core with the cross sectional area of both the sheath and the core being 50% of the cross sectional area of the monofilament. The monofilament was extruded and conditioned as in

Example 3, and processed into brushes. The ends of the monofilament were abraded with a stainless steel brush as in Example 3. No pocket was formed in the ends of the monofilaments, and the ends had a normal rounded appearance such as is shown in Figure 3.

5

WHAT IS CLAIMED IS:

1. A coextruded monofilament comprising:

a core material of a first resin,

a sheath material of a second resin, said second resin being different from said first resin, and

a pocket formed in the end of the monofilament.

2. The coextruded monofilament of claim 1, wherein sheath material is nylon 6; nylon 6,6; nylon 6,10; nylon 6,12; nylon 6,9; nylon 11; nylon 12; copolymers of nylon 6 and nylon 6,6; 10,10 nylon; and mixtures thereof, and the core material is a copolyester ether.

3. The coextruded monofilament of claim 1, wherein the sheath material is a nylon, a polyester, a polyurethane, polyvinylidene chloride, or mixtures thereof, and the core material is a polyvinyl chloride, polyvinyl acetate copolymer, polystyrene, or mixtures thereof.

4. The coextruded monofilament of claim 1, wherein the sheath material is nylon 6, 10 or nylon 6, 12, and the core material is nylon 6, nylon 6,6, nylon 6,10 or polybutylene terephthalate.

5. The coextruded monofilament of claim 1, wherein the cross-sectional area of the core material comprises from about 10 to about 90% of the cross-sectional area of the monofilament.

6. The coextruded monofilament of claim 1, wherein the cross-sectional area of the core material comprises from about 25 to about 75% of the cross-sectional area of the filament.

7. The coextruded monofilament of claim 1, wherein the depth of the pocket is from about 0.001 to about 0.250 inches from the end of the monofilament.

8. The coextruded monofilament of claim 1, wherein the cross sectional shape of the sheath is circular, triangular, square, pentagonal, hexagonal, oval, lobate, triocular or tetraocular.

9. The coextruded monofilament of claim 1, wherein the cross sectional shape of the sheath is circular, triangular, square, pentagonal, hexagonal, oval, lobate, triocular or tetraocular.

10. The coextruded monofilament of claim 1 wherein the ends of the coextruded monofilament are flagged.

11. A bundle comprising a plurality of the coextruded monofilaments of claim 1.

12. A brush comprising a handle associated with a head having a least one tuft attached to the head, said tuft comprising a plurality of the monofilament of claim 1.

13. A method for forming a pocket in the end of a coextruded monofilament comprising the steps of providing a monofilament having a core material of a first resin and a sheath material of a second resin, said second resin being different from said first resin, and

abrading the core of the monofilament to form a pocket in the end of the monofilament.

14. A method for forming a pocket in the end of a coextruded monofilament comprising the steps of providing a monofilament having a core material of a first resin and a sheath material of a second resin, said second resin being different from said first resin, and

bringing the end of the monofilament in contact with a solvent that dissolves the core material but not the sheath material to form a pocket in the end of the monofilament.

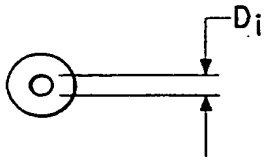

FIG.2

FIG.4

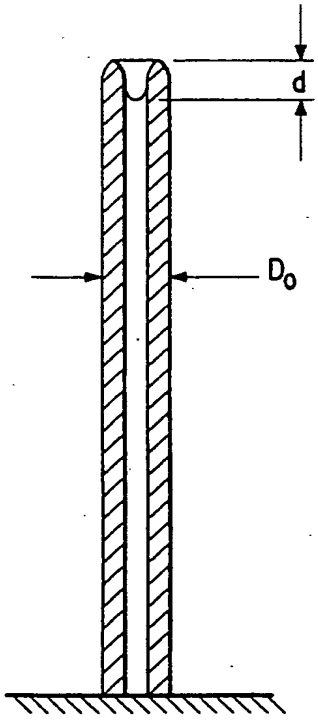

FIG.1

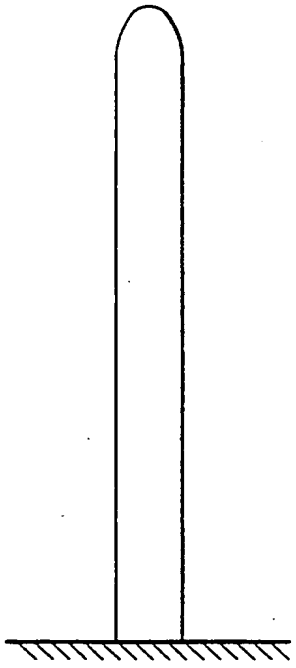

FIG.3

FIG.5

FIG.6

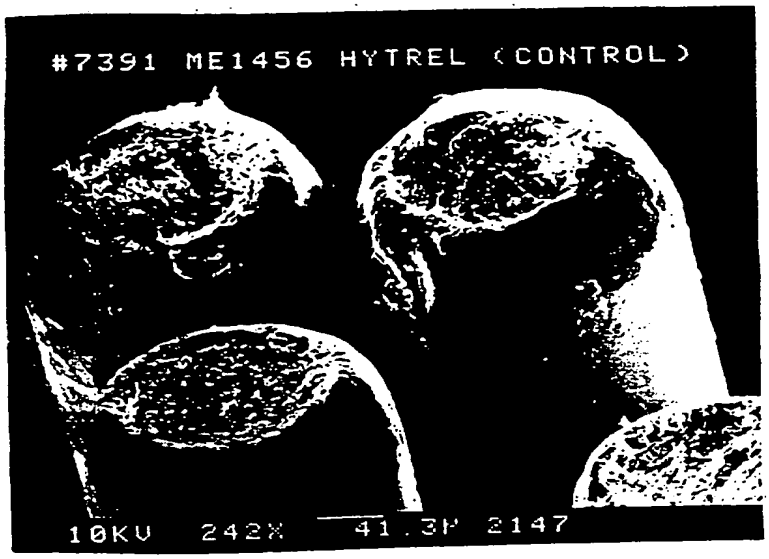

FIG.7

FIG.8


#7415 ME1456 AD12A GY 154
10KV 158X 63.3M 2138

FIG.9

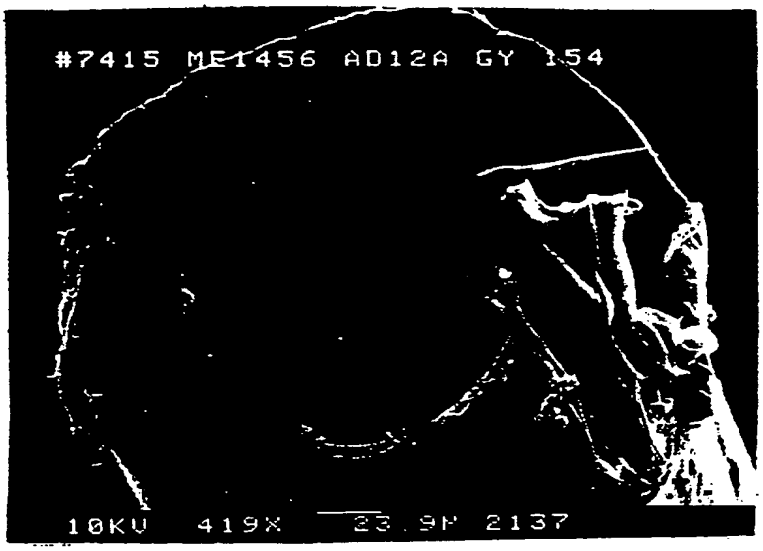
#7415 ME1456 AD12A GY 154
10KV 419X 23.9M 2137

FIG.10

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/16293

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D01F8/04 D01F8/12 D01F8/14 A46D1/00 D01D5/253

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D01F A46D D01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	PATENT ABSTRACTS OF JAPAN vol. 96, no. 7 & JP,A,08 187126 (TOYOBO CO LTD), 23 July 1996, see abstract ---	1-14
A	PATENT ABSTRACTS OF JAPAN vol. 95, no. 009 & JP,A,07 231813 (TOYOBO CO LTD), 5 September 1995, see abstract ---	
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 451 (C-1241), 23 August 1994 & JP,A,06 141928 (HIROSHI FUKUBA), 24 May 1994, see abstract ---	
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 January 1997	10.02.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Tarrida Torrell, J

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Ir tional Application No
PCT/US 96/16293

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 285 (C-0851), 19 July 1991 & JP,A,03 099604 (TORAY IND INC), 24 April 1991, see abstract	
A	EP,A,0 663 162 (PROCTER & GAMBLE) 19 July 1995	
A	US,A,5 313 909 (TSENG MINGCHIH M ET AL) 24 May 1994 cited in the application	

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int ional Application No
PCT/US 96/16293

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0663162	19-07-95	WO-A-	9519120	20-07-95
US-A-5313909	24-05-94	AU-A-	5457594	24-05-94
		CN-A-	1097969	01-02-95
		EP-A-	0668991	30-08-95
		JP-T-	8503145	09-04-96
		WO-A-	9410539	11-05-94
		ZA-A-	9308022	28-06-94